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Cryptoendolithic alteration of Antarctic sandstones: Pioneers or opportunists?

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[1] The cryptoendolithic habitat of the Antarctic Dry Valleys has been considered a good analogy for past Martian ecosystems, if life arose on the planet. Yet cryptoendoliths are thought to favor the colonization of rocks that have a preexisting porous structure, e.g., sandstones. This may weaken their significance as exact analogues of potential rock-colonizing organisms on Mars, given our current understanding of the dominant volcanic nature of Martian geology. However, the production of oxalic acid, by these lichen-dominated communities, and its weathering potential indicate that it could be an aid in rock colonization, enabling endoliths to inhabit a wider variety of rock types. Utilizing ICP-AES and scanning electron microscope techniques, this study investigates elemental and mineralogical compositions within colonized and uncolonized layers in individual sandstone samples. This is in order to determine if the weathering of mineral phases within the colonized layers causes an increase in the amount of pore space available for colonization. The results show that colonized layers are more weathered than uncolonized, deeper portions of the rock substrate. Layers within uncolonized samples have uniform compositions. Differences between the colonized and uncolonized layers also occur to varying extents within colonized rocks of different mineralogical maturities. The results confirm that cryptoendoliths modify their habitat through the production of oxalic acid and suggest that over time this directly increases the porosity of their inhabited layer, potentially increasing the biomass it can support.

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1. Introduction

[2] Cryptoendolithic communities from the McMurdo Dry Valleys of Antarctica have been proposed as potential analogues of Martian life-forms [Friedmann, 1982; Friedmann and Ocampo-Friedmann, 1984b; McKay, 1993; Wynn-Williams and Edwards, 2000a, 2000b]. This is primarily owing to the stress tolerant nature of the micro-organisms, their adaptive characteristics and the similarities between Antarctic Dry Valley ecosystems and assumed conditions at the Martian surface. The Antarctic Dry Valleys have been considered the closest terrestrial analogue of Mars since the Viking missions of the 1970s [Friedmann and Ocampo-Friedmann, 1984b]. This comparison is particularly relevant to two periods in Mars' history ~ 3.8 – 3.1 and ~ 3.1 – 1.5 Gyr ago defined as Epoch II and Epoch III respectively. McKay *et al.* [1992] postulated that during Epoch II mean annual temperatures would have fallen below freezing but peak seasonal

temperatures could have been above freezing so liquid water would exist in equilibrium with ice, e.g., ice-covered lakes analogous to those in Antarctica. Epoch III is defined as the period where mean and peak temperatures would have been below 0°C (273 K), pressure would have been high enough (>6.1 mb) to support liquid water but the water would only have been transient [McKay *et al.*, 1992]. This is a similar climatic condition to that that occurs in the elevated (>1000 m altitude) McMurdo Dry Valleys of Antarctica today [McKay *et al.*, 1992]. The evolution and adaptation of life in the Antarctic environment therefore is of particular relevance to astrobiological studies of the planet Mars.

[3] The McMurdo Dry Valleys, or Ross Desert, is an extensive ice-free region of around 4800 km^2 that sits inside the Transantarctic Mountains lying between 160° and 164°E , and $76^{\circ}30'$ and $78^{\circ}30'\text{S}$. The region is especially arid, owing to dry polar winds that descend from the Antarctic ice plateau across the valleys. High UV-B irradiance levels, low temperatures and lack of water are a combination of extreme environmental stresses unique to this deglaciated terrestrial environment [Onofri *et al.*, 2004]. Yet cryptoendoliths (hidden-within-rock) exist, surviving in protected niches. The major limiting factors of temperature, water availability and UV radiation are overcome because the endolithic environment is an internal microscopic habitat upon which outside conditions have only limited

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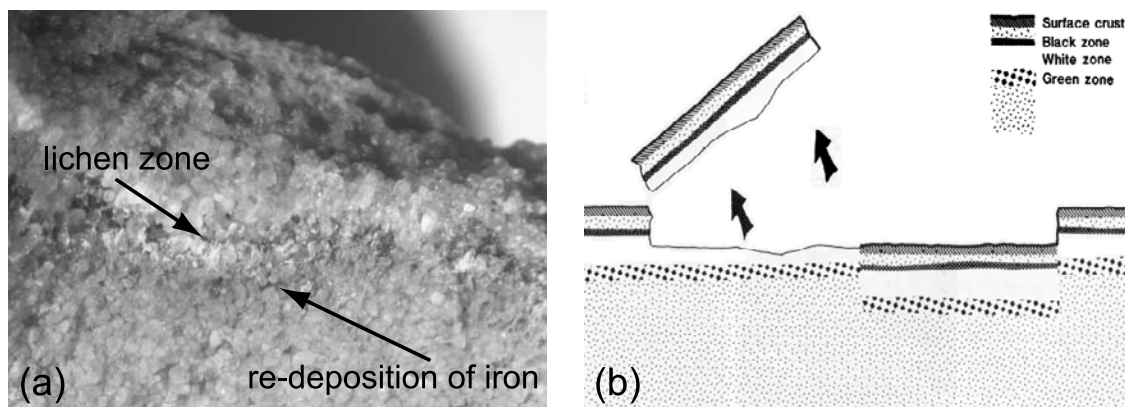


Figure 1. (a) Typical cryptoendolith-bearing sandstone, showing the different layers and effect of the mobilization of iron compounds leached from the colonized layer and redeposited below or above it and (b) a schematic diagram of the exfoliation of the surface crust [after *Friedmann, 1982*] caused by the dissolution of cements between the mineral grains leading to gradual exfoliation of the surface crust, which in turn apparently regulates the cryptoendolithic habitat. Exfoliation events occur when the microbial biomass reaches the carrying capacity of the rock [Sun and *Friedmann, 1999*].

influence [*Friedmann, 1980*]. These organisms are thought to have descended from early, preglaciation Antarctic life-forms and as such could represent the last surviving life in a gradually deteriorating environment [*Friedmann and Ocampo-Friedmann, 1984b*]. This has made them a suitable analogy for past Martian ecosystems, assuming life arose on the planet during an earlier, less hostile era.

[4] This comparison is especially applicable to the period of the Mars' history (Epoch III ~3.1–1.5 Gyr ago) previously described. During this period, any microbial colonies that had evolved during earlier, more temperate periods would not necessarily have become extinct, but instead might have retreated into porous and translucent rocks, such as sandstones. Here they might have survived with solar heating on the surfaces of the rocks creating rock temperatures of over 15°C, forming microscopic greenhouse conditions [*McKay et al., 1992*]. The effect of solar heating may also have caused periodic snowfall to melt and percolate into the rock interior where it could be held in the air space system after ambient humidity had fallen to low values [*McKay et al., 1992*]. The translucent nature of the rocks would also have allowed sunlight to penetrate the upper few millimeters of the substrate enabling photosynthetic metabolism. Such a habitat would provide an insulated, protected niche within an extreme and inhospitable macroenvironment. Conditions inside the rocks would be comparatively mild, contrasting with the abiogenic exterior surfaces.

[5] Cryptoendolithic communities are principally composed of photosynthetic microorganisms and fungi, however some can be dominated by eukaryotic organisms while others can be formed entirely of prokaryotes [*Friedmann et al., 1988*]. Though it is the cyanobacterial components of the communities that are thought to be prime candidates for the potential colonization of the surface of early Mars [*Wynn-Williams and Edwards, 2000a*], it is cryptoendolithic lichen that dominate the communities in the Antarctic environment. This is owing to their ability to exist in a “freeze dried” state, that apparently does not damage cellular structures, during winter or in absence of direct

insolation and their utilization of water vapor for metabolism rather than requiring the presence of liquid water as their cyanobacteria-dominated hot desert counterparts do [*Friedmann, 1980*].

[6] It is not known whether that upon the emergence of putative prokaryotic life on Mars that the timeframe exists for the subsequent evolution of eukaryotic life. However, Mars is thought to have undergone similar geological evolutionary processes as did the early Earth but with the advantage of having a 50% smaller diameter giving a fourfold larger surface-area-to-volume ratio for heat loss, being a greater distance from the Sun thus receiving less thermal input and not undergoing the hiatus of the Moon-forming impact that remelted the crust of the Earth [*Wynn-Williams et al., 2002*]. Mars therefore may have cooled to a suitable temperature for a biosphere quicker than the Earth and may have evolved a microbiota in advance of the Earth, with a potential for Panspermia inoculation [*Wynn-Williams and Edwards, 2000b*].

[7] Cryptoendolithic lichens may therefore be relevant to early exobiology on Mars as well as being instrumental in the future colonization of Mars as proposed in ideas for the possible ecosynthesis of the planet [*Graham, 2003, 2004*].

[8] Cryptoendoliths preferably colonize rocks that have a porous structure, like sandstones, because they do not penetrate the substrate by solution [*Friedmann, 1982*]. This may therefore weaken their significance as exact analogues of potential rock-colonizing organisms on Mars, given our current understanding of the dominant volcanic nature of Martian geology with volcanogenic sediments being prevalent [*Parnell, 2004*]. However, cryptoendolithic lichens interact with the substrate they inhabit by producing oxalic acid [*Johnson and Vestal, 1989, 1993; Edwards et al., 1997; Russell et al., 1998; Wynn-Williams and Edwards, 2000a*]. Studies have shown that the mobilization of minerals is attributed to the production of oxalates, which arise from oxalic acid produced by fungal hyphae [*Johnson and Vestal, 1989, 1993; Edwards et al., 1997*]. Mineral dissolution and mobilization provides the communities with nutrients but in addition has been shown to cause

characteristic bio-weathering patterns (see Figures 1a and 1b) [Friedmann, 1982; Friedmann and Ocampo-Friedmann, 1984a; Friedmann and Weed, 1987; Johnson and Vestal, 1993; Sun and Friedmann, 1999], the destruction and creation of rock crusts [Friedmann and Weed, 1987; Johnson and Vestal, 1993; Sun and Friedmann, 1999], regulation of the biological residence time of the community [Friedmann and Weed, 1987; Sun and Friedmann, 1999], and the creation of inorganic biomarkers and formation of microbial fossils [Friedmann and Weed, 1987; Wierzbos and Acasco, 2001, 2002; Acasco and Wierzbos, 2002, 2003; Wierzbos et al., 2003]. These characteristics of the cryptoendolithic habitat make them good natural samples to analyze in order to develop suitable techniques for future application to Martian samples in the search for analogous Martian life-forms [McKay, 1993].

[9] In addition to these effects of oxalate on the substrate, it has been suggested that oxalate weathering has the potential to enlarge the pores of the substratum developing the endolith habitat and therefore increasing its habitability [e.g., Wynn-Williams and Edwards, 2000a]. This potentially could act as an aid in rock colonization enabling endoliths to inhabit more diverse, less porous rocks. The ability to colonize a wider variety of habitats would make cryptoendolithic communities pioneering organisms which would make them better suited as analogues for Martian microorganisms.

[10] Clear compositional differences occur between colonized and uncolonized sandstone samples from the Antarctic Dry Valleys. These differences indicate significant alteration of the colonized rocks by the cryptoendolithic microorganisms [Blackhurst et al., 2004]. This data, however, does not clarify whether the chemical and mineralogical differences were a secondary feature, i.e., the result of cryptoendolith action, or whether they were a primary feature of the different rock types.

[11] To take account of inherent differences in mineralogy between rocks from different locations, and to determine if the weathering of mineral phases within the inhabited layers creates additional pore space, we have undertaken a study to compare the major elemental and mineralogical compositions of individual layers within endolith-bearing sandstones.

2. Materials and Methods

[12] Cryptoendolithic communities form distinctive biotic zonations under the surfaces of the sandstones they inhabit. In the Antarctic Dry Valleys, all zones are produced by filamentous fungi and unicellular green algae (Chlorophyceae) [Friedmann, 1982]. A typical cryptoendolith profile consists of a siliceous rock crust followed by a black zone made up of dark pigmented fungi that enclose algal cells (forming a lichen association), followed by a white zone consisting of colorless fungal hyphae, and then a green zone predominantly made up of the green alga *Hermichloris antarctica* [Friedmann et al., 1988]. Other microorganisms may occasionally occur in this green zone, e.g., colorless fungal hyphae without forming a lichen, the cyanobacterium *Chroococcidiopsis* sp., and much less frequently the large cyanobacterium *Gloeocapsa* sp. Definite, vertical zonation occurs between the different photosynthetic organisms when

present, though this is not visually obvious [Friedmann et al., 1988]. Below the green zone may be a red layer of redeposited iron compounds immediately above the uncolonized rock substrate [Friedmann, 1982].

[13] A steep light intensity gradient exists in the upper few millimeters of the rock. Light penetration into the rocks has been shown to vary with (1) depth within the rock, amounting to an order of magnitude decrease per mm, and (2) moisture, amounting to an order of magnitude increase when the rock is wet [Nienow et al., 1988; Vestal, 1988a, 1988b]. The amount of light penetrating the biotic zone has been estimated at ~ 0.02 – $20 \mu\text{mol}$ of photons per m^2 per s on the basis of the maximum ambient light intensity of about 1800 – $2000 \mu\text{mol}$ of photons per m^2 per s on a sunny day at Linnaeus Terrace in the Dry Valleys, Antarctica ($77^{\circ}36'S$, $161^{\circ}05'E$) [Vestal, 1988a]. Under these light conditions and when the rock is wet, the communities are exposed to ~ 0.2 – $200 \mu\text{mol}$ of photons per m^2 per s, thus an average light intensity would therefore be about 2 – $20 \mu\text{mol}$ of photons per m^2 per s around 2 – 3 mm below the rock surface [Vestal, 1988a]. Optimum light intensity for photo-metabolism has been shown to be about 200 – $300 \mu\text{mol}$ of photons per m^2 per s, though light intensities of around 1 – $10 \mu\text{mol}$ of photons per m^2 per s are still suitable for photosynthesis [Vestal, 1988b]. The sharp boundaries of the inhabited layers, which define the colonized cryptoendolith zone, are probably a result of this steep light intensity gradient existing in the upper few millimeters of the rock [Friedmann, 1980]. It is therefore easy to differentiate between layers that are colonized and those that are not. This allows a comparison of colonized and uncolonized layers to be conducted within the same sample.

2.1. Specimens

[14] Suitable samples were selected from the suite of rocks used in the study of Blackhurst et al. [2004]. The samples are Devonian age (395 – 345 Ma) quartz and feldspathic arenite sandstones from the Beacon Supergroup collected by a British Antarctic Survey expedition to Terra Nova Bay and McMurdo Base during the Antarctic summer of 1995 – 1996 [Edwards et al., 1997]. The samples used in this study were initially sampled for biological analyses and stored from collection in a freezer at -5°C at the British Antarctic Survey. They were relocated to the Natural History Museum in London in 2002 to be used for mineralogical and chemical analyses and were then stored under dry environment conditions at room temperature.

[15] Three samples were selected from the suite, each representing a different level of mineralogical maturity (Figures 2a–2c): EB1 (mature, e.g., dominated by quartz; colonized); MM45 (immature, e.g., dominated by alkali feldspars; uncolonized) and TP1 (intermediate, e.g., containing quartz and alkali feldspars; colonized). The immature uncolonized sample acted as a control. It is postulated that the reason the samples from Mount Mackintosh are uncolonized is owing to this site's aspect and exposure. While the sites from which the colonized rocks were sampled from face north and have sheltered exposures, the site at Mount Mackintosh is west facing and is exposed to the plateau [Russell et al., 1998]. Extreme xeric conditions owing to the full force of polar Katabatic winds may be the cause of the lack of colonization at this site [Russell et al., 1998].

[16] The study involves a comparison of the layers within each individual sample; however, an overall comparison will be drawn between the three samples to ascertain if there are any variations that occur within layers between rocks of different mineralogical maturity.

[17] Any one or more of the layers of the distinct vertical sequence of black, white and green zones may be absent from cryptoendolith-bearing rocks [Friedmann, 1982]. The colonized samples selected for this study do not contain the green zone. The layers selected for analysis in both of the colonized samples are the crust (CR), the colonized layer (CL), a red-colored layer of iron redeposition (RD) and a layer of the deeper rock substrate (SB). In the uncolonized sample there are no defined layers, so layers corresponding to the depths of those defined in the colonized samples were analyzed. Details of the samples and their localities are given in Table 1.

2.2. Electron Microscopy

[18] Gross mineralogical differences between whole rock specimens of the three samples have been established [Blackhurst et al., 2004] (Figures 2a–2c). To ascertain if there were any mineralogical differences between specific layers within a single sample, percentages of the mineral phases present were determined in individual layers. The depths of the layers selected for phase map analyses correspond to the thicknesses of the layers of interest in the rock samples. In the two colonized rocks, the micro-organisms do not appear to be present below a depth of ~5 mm. The original rock substrates begin at depths of ~5 mm. The crusts are ~1 mm thick and the colonized and iron-rich layers are a thickness of ~2 mm each. The rock substrates under the iron-rich layers are several millimeters thick but for consistency the layers were analyzed at a thickness of ~2 mm. For the uncolonized sample, layers were analyzed at depths corresponding to those defined in both colonized samples. Phase mapping was conducted on carbon coated polished thin sections (30 μ m) using a LEO 1455 variable pressure scanning electron microscope operating at 20 kV under high vacuum with a working distance of 15 mm. Automated photo montage and qualitative elemental mapping was carried out using Oxford Instruments INCA system on the LEO 1455. Each photo montage consisted of a composite series of images of each thin section obtained at a magnification of $\times 200$ and a resolution of 512×398 pixels.

[19] Major elemental compositions were obtained by energy dispersive X-ray mapping. The LEO is capable of quantitative analysis with an accuracy of $\pm 0.5\%$ for major elements. Major elemental concentrations were determined using INCA microanalyzer software. Combinations of specific elements could be associated with specific minerals; each phase was allocated a color for identification, and apparent mineral abundances calculated from the color maps. No preferred mineral grain orientation was observed, thus the area of a phase measured in a section approximates closely to its volumetric abundance.

2.3. Chemical Analysis (ICP-AES)

[20] Major element chemistries of the samples were measured by ICP-AES using a JY24 Sequential Spectrometer at Kingston University. The instrument was set up for

the determination of the major rock forming elements in the silicate minerals present in the samples, e.g., Al, K, Na, Fe, Ca, Mg, plus P and Mn which previous studies have shown are mobilized by oxalate and leached from the lichen layer [Johnson and Vestal, 1989, 1993]. The precision of the ICP-AES instrument is 0.5–1% or better for major element analysis. Detection limits for most elements were between 0.2 and 25 ppb in the sample. Grains were handpicked from each layer, homogenized using an agate pestle and mortar and then dissolved using an HF-HClO₄-HNO₃ acid digestion procedure. Silica is lost to the vapor phase during acid digestion. Calibration standards BCR-1 (basalt); NIM-G (granite); MESS2 (marine mud); STM1 (nepheline syenite); AGV1 (andesite); W2 (dolerite); ACE (granite); AW11 (shale); KH2 (limestone); and JLS1 (Japanese limestone) were run through the same procedure to calibrate the instrument.

3. Results

3.1. Electron Microscopy–Phase Map Analysis

[21] The results of the phase map analyses are shown in phase map micrographs in Figures 3a–3c, percentages of the mineral phases are plotted in Figure 4 and are also given in Tables 2–4. The immature uncolonized sample, MM45, acted as a control. As can be seen from both Figures 3a and 4 and Table 2, the compositions of the layers in this sample are very similar, with only minor differences between them. There is no systematic change in mineral abundances with depth below the surface of the sample.

[22] Data for TP1, the sample of intermediate mineralogical maturity, are given in Table 3, plotted in Figure 4 and phase map micrographs are shown in Figure 3b. As can be seen, the abundance of various minerals present in the sample varies between layers. Alkali feldspars (both K and Na) increase with depth below the colonized layer of the sample, whereas the percentage of quartz (SiO₂) decreases. The abundance of quartz is approximately inversely proportional to alkali feldspar. The colonized layer (CL) contains the least alkali feldspar, less than the deeper rock substrate (SB). Kaolinite clay in this sample is lowest in the crust (4%) and highest in CL (~9%) and SB (~10%). There are similar porosities in layers CR, CL, RD and SB.

[23] Data for EB1, the mature colonized sample, are given in Table 4, plotted in Figure 4 and phase map micrographs are shown in Figure 3c. This sample is the most mature mineralogically out of the three samples in that it is fairly homogenous, composed of predominantly quartz with some kaolinite clay. Feldspars were not detected in this sample. Despite its maturity, however, differences still exist between the different layers, most prominently between CL and SB. As in sample TP1, CL has a greater amount of quartz than SB (which has the least). Kaolinite clay is found in the highest concentration in SB and least in CL. CR and RD have comparable amounts of kaolinite. Pore space in this sample is greatest in CL and least in SB.

3.2. Chemical Analysis

[24] Major elemental abundances from ICP-AES analyses within the separate layers in each sample are shown in Figure 5. Figure 5a shows the results for MM45 which acted as a control. The upper and lower portions of the sample are

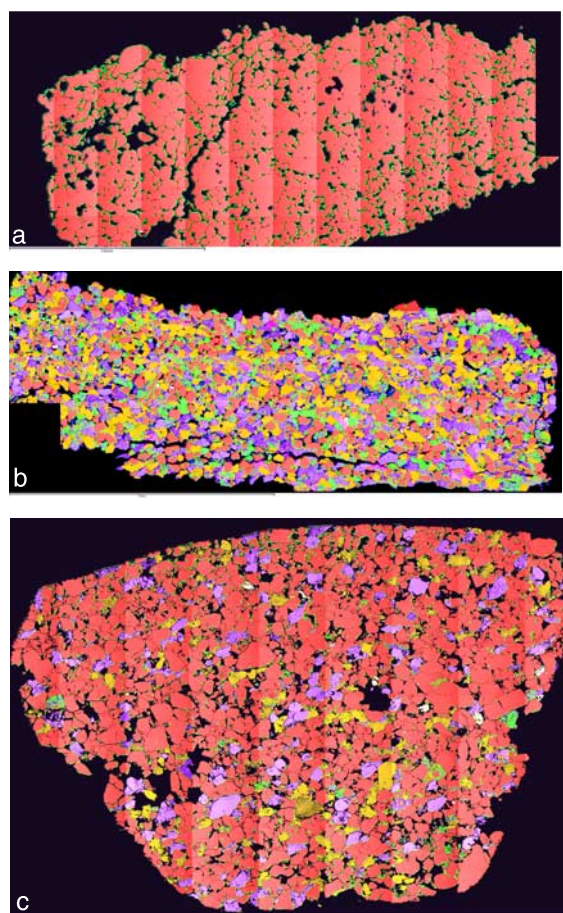


Figure 2. Montage and element map micrographs of the three samples showing the mineral phases determined within them. These demonstrate the overall mineralogical differences between samples. (a) EB1, (b) MM45, and (c) TP1. Mineral phases are shown in red (quartz), purple (K-feldspar), orange (Na-feldspar), and green (kaolinite).

comparable, with only minor differences between them. Manganese is found in both layers at ~ 164 ppm in the lower layer and ~ 256 ppm in the upper layer. In comparison manganese was not present in detectable amounts in any of the layers of sample EB1 or in the colonized layer of sample TP1 and was only found in very small amounts in the other layers of TP1. Generally, the upper layer of MM45 has slightly higher concentrations (by a factor of ~ 1.35) than the lower, except for K. The lower layer has 1.07 times the concentration of K than the upper layer.

[25] Figure 5b shows the results for intermediate colonized sample TP1. Differences in the concentrations of elements Al, Ca, Mg, Mn, Na K, Fe and Ti are clear between the layers within this sample. Concentrations of these elements are greater in SB than in the colonized layer on average by a factor of 4.4 and range from as high as a

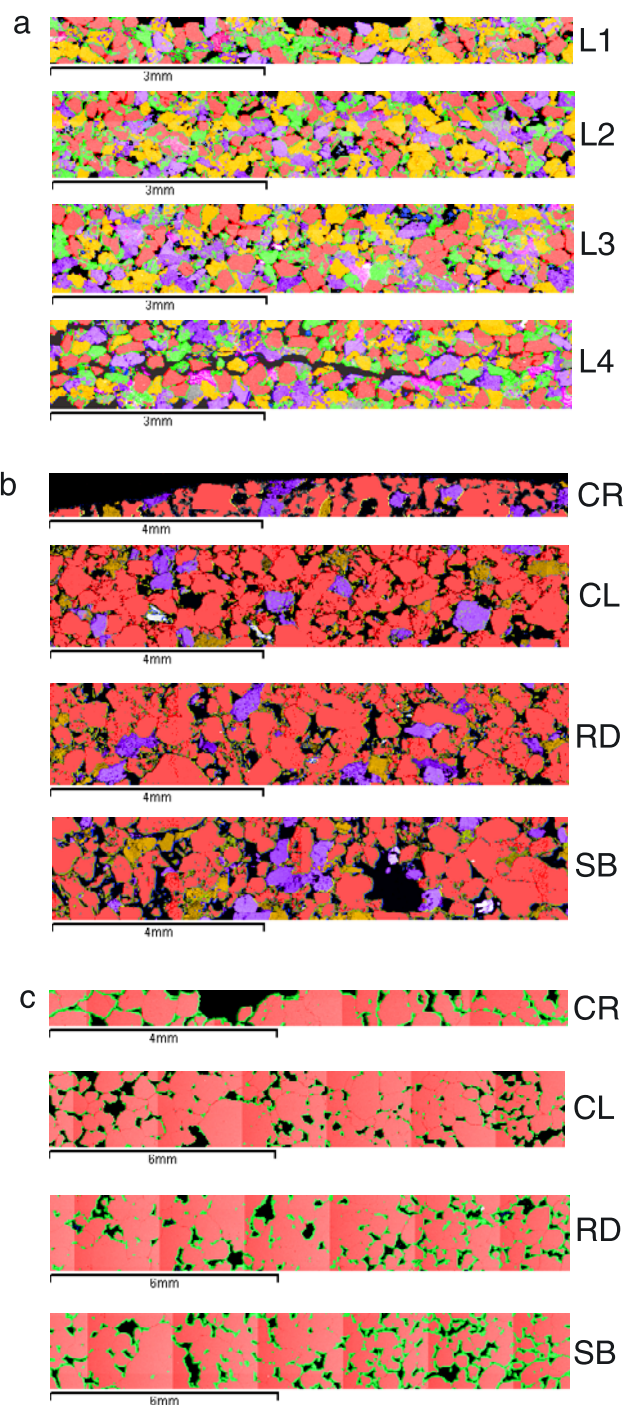


Figure 3. Phase map micrographs of individual layers within the samples. (a) MM45, (b) TP1, and (c) EB1. For EB1 and TP1, CR is crust; CL is colonized layer; RD is layer of iron redeposition; SB is substrate. For MM45, L1 is the outermost layer (crust), and L4 is the innermost. Mineral phases are shown in red (quartz), purple (K-feldspar), orange (Na-feldspar), and green (kaolinite).

Table 1. Samples and Field Localities

Sample	Locality	Grid Reference	Altitude, m	Maturity	Status
EB1	East Beacon Mountain	77°50'S 160°52'E	2200	mature	colonized
TP1	Timber Peak, East Plateau	74°10'S 162°30'E	2800	intermediate	colonized
MM45	Mount MacKintosh	74°40'S 161°45'E	2100	immature	uncolonized

factor of 8.5 (Fe) to as low as a factor 2.94 (K). Calcium is found in all the layers of this sample and 3.8 times the amount is found in SB than in CL. There is no detectable manganese in CL, but trace amounts are found in the other layers, ~ 20.3 ppm in both RD and CR and 10.1 ppm in SB. In TP1, iron has the highest concentration in RD, approximately 23 times the amount found in CL. CR has the second highest concentration ($\sim 10 \times$ CL), followed by SB ($\sim 8.5 \times$ CL).

[26] Figure 5c shows the results for mature colonized sample EB1. Differences in the concentrations of elements Al, Ca, Mg, Mn, Na K, Fe and Ti can be seen between the layers in this sample with SB, in most cases, containing higher concentrations of these elements. Major elemental concentrations are greater in SB than in CL on average by a factor of 2.6, ranging from as high as a factor of 4.3 (Fe) to as low as a factor of 1.3 (Ti). An exception is calcium, which is only found in detectable concentrations in CL (~ 222 ppm). There is no detectable manganese in any of the layers and magnesium concentrations are comparable in SB and CL at ~ 37.9 ppm and ~ 37.7 ppm respectively. Iron is highest in SB followed by CR and RD; it is lowest in CL.

4. Discussion

4.1. Weathering Processes in the Antarctic Dry Valleys

[27] Mineralogical and mineral chemistry differences within and between layers in sandstone samples can be viewed in the context of observations that have been made of a combined abiogenic and biogenic weathering cycle. Previous studies, e.g., *Friedmann and Weed* [1987], have suggested that the outer crust of sandstone boulders is subject to abiogenic weathering that can be either preservative or destructive. Preservative abiogenic weathering occurs when a siliceous crust is formed by accumulation of airborne particulate matter composed of quartz, clays and Fe oxyhydroxides. These coat and fill the pore spaces between near-surface grains. SiO_2 fills the pore spaces by precipitation of quartz that is optically continuous with the sandstone grains forming resistant quartz rinds. In contrast, destructive weathering processes that occur on the surface crust include salt weathering, grain by grain disintegration by frost, salt or wind action, and polishing by aeolian abrasion.

[28] Biogenic weathering of the crust occurs as a result of cryptoendolith colonization. Cyclic exfoliation of the surface crust is caused by dissolution of cement between crystals in the colonized layer by the oxalic acid produced by the organisms [*Friedmann and Weed*, 1987; *Sun and Friedmann*, 1999]. This results in the loss of the protective rock layer, causing exposure of the endoliths that then disperse and, in most circumstances, die. The organisms at the base of the exposed layer infiltrate pore spaces in the deeper rock substrate, recolonizing at an optimum level of temperature and light intensity. The rock crust is now an exposed area of white, leached sandstone and over time a new siliceous crust forms on this surface [*Friedmann and Weed*, 1987]. Meanwhile, oxalic acid produced by the microbes leaches metals from the new lichen-dominated layer, resulting in mobilization of major and minor elements; soluble oxalate complexes are carried from the lichen layer into deeper layers, by water from snowmelt or up toward the surface by capillary action as the rock

dries, thus depleting the lichen zone of major elements [*Johnson and Vestal*, 1993]. Dissolved silica complexes could in the same way move both upward by capillary action and downward into the rock. Near the surface of the rock where the intensity of sunlight is optimal oxalate should photo-oxidize to release free monomeric silica. Thus amorphous silicates or clay minerals would precipitate becoming part of the siliceous crust at the surface of the rock [*Johnson and Vestal*, 1993].

4.2. Differences Within Samples

[29] Mineralogical and mineral chemistry data for immature uncolonized sample MM45 indicate a uniform substrate with depth (Figures 3a, 4, and 5a and Table 2). This uniformity is as would be expected from a rock subject to abiogenic weathering processes. The slight disparity between upper and lower layers (i.e., upper layer having on average 1.35 times the concentration of elements than the lower layer) probably arises because the upper layer is more subject to aeolian deposition of quartz, clays and Fe oxyhydroxides, that help form the siliceous crust.

[30] For both colonized samples, the mineralogy and mineral chemistry of CL are more altered than the other layers, in particular the uncolonized portions that represent the deeper rock substrate (SB). This is most evident in TP1 (Figures 3b, 4, and 5b and Table 3): it contains a higher concentration of the feldspar minerals that are more readily weathered than quartz. The greatest difference is seen between SB and CL. High kaolinite in CL is probably the result of weathering of feldspars to clays. This may indicate that the microbes are in the process of weathering minerals in this layer which potentially will create more pore space. The colonized layer, however, in this sample has the lowest porosity. This might be because feldspar weathering would not initially create more pore space: feldspars are not removed, but are converted to clay minerals that at first remain in situ. Eventually these clays may be moved out of the layer. Oxalate-enhanced mobilization, transportation, and reprecipitation of silica should occur as it does for metals [*Johnson and Vestal*, 1993].

[31] Sample EB1 has a very mature mineralogy, consisting mainly of quartz with some kaolinite. This could either be a primary lithological feature of the sample or it could have attained this high level of maturity through an abiogenic weathering process acting on the whole substrate. However, despite its maturity, differences are still seen between CL and the other layers. Like sample TP1, SB is inclined to have higher concentrations of the elements Al, Ca, Mg, Mn, Na K, Fe and Ti than the other layers. The greatest difference is seen between SB and CL. Phase map data (Figures 3c and 4 and Table 4) show that the colonized layer has the highest percentage of quartz ($\sim 82\%$), lowest kaolinite ($\sim 9\%$) and highest pore space ($\sim 10\%$). In contrast the deeper rock substrate has the lowest amount of quartz ($\sim 76\%$), highest kaolinite ($\sim 20\%$) and least pore space ($\sim 4\%$).

4.3. Differences Between Samples

[32] The data set reflects the differences in the mineralogy amongst all three samples, as well as differences within a single sample. A comparison can be made between colonized samples TP1 and EB1 and uncolonized sample MM45

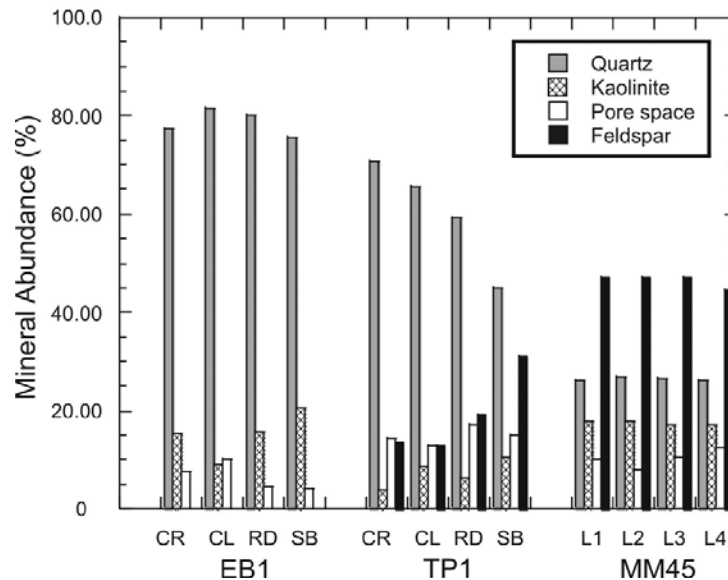


Figure 4. Histogram of EB1, TP1, and MM45 showing the percentages of phases determined in each layer. For EB1 and TP1, CR is crust; CL is colonized layer; RD is layer below colonized layer into which iron is redeposited; SB is substrate. For MM45, L1 is the outermost layer (crust), and L4 is the innermost.

showing overall differences in chemistry between them. Concentrations of elements in TP1 are, on average, higher than in EB1 by a factor of 11. Concentrations of elements in uncolonized MM45 are, on average, higher than in TP1 by a factor of 8 and higher than in EB1 by a factor of 58.

[33] It is known from the mineralogy that silica features in high concentrations because quartz is the dominant mineral in sandstones. In EB1, silica is found in a higher concentration than other major elements, e.g., Al, Na, and K, which primarily make up feldspars. In contrast, in MM45, elements found in feldspars are in higher concentrations than silica. Silica then, is found in higher concentrations with increasing maturity of sample (e.g., EB1 > TP1 > MM45), while Al, Na and K occur in higher concentrations with decreasing maturity.

4.4. Crust Development in Colonized Samples TP1 and EB1

[34] Different stages of crust development in TP1 and EB1 could be indicated by the results of this study. A comparison can be made between the amounts of clay minerals in CL in EB1 and of CL in TP1. The percentage of kaolinite in the colonized layer in EB1 is the lowest of all the layers but pore space is found to be the highest. The kaolinite content in the crust of EB1 is considerably higher than in CL, and also about 3.5 times more than in the TP1 crust. This may indicate that EB1 is at a more advanced stage of the biogenic weathering cycle described above, and that clays created by the weathering of feldspars in CL have become part of the developing crust. The crust is subject to periodic exfoliation, and when this occurs the colonized layer effectively becomes the new crust. Over time, a new siliceous crust develops on this surface. By comparing the crust data for TP1 and EB1, it could be argued that EB1 is at a later stage of crust development after such an exfoliation

event and TP1 is at an earlier stage. For example, kaolinite is found in its lowest percentage in TP1's crust while it is found in its lowest percentage in EB1's colonized zone. Pore space in TP1's crust is twice that of pore space in EB1's crust. If TP1's crust was once the colonized layer then the lack of kaolinite and greater pore space could be attributed to past cryptoendolith action. Subsequent exfoliation caused TP1's colonized layer to become the new crust. So crust mineralogy is influenced by (1) abiogenic aeolian weathering processes, (2) mobilization and precipitation of amorphous silicates and clay minerals, and (3) cryptoendolith exploitation when the crust was colonized by the microbes during a previous period.

[35] Sample EB1 therefore may have been colonized by the organisms for a significantly longer time period than TP1. Certainly the EB1 crust data suggest that it is at a later stage of development owing to the greater percentage of SiO₂, clays and low pore space. It implies that exfoliation of the previous crust occurred a considerable time ago. The growth of the microbial communities inside the rock and dissolution of cement between crystals in the colonized layer, which leads to exfoliation events, occur on the same timescales of around 10³–10⁴ years [Sun and Friedmann, 1999]. The exfoliation of the surface crust of TP1 may have occurred more recently, and so new crust is still developing.

[36] The results of this study reveal that compositional differences occur between individual layers within samples that are colonized by cryptoendolithic microorganisms. The most pronounced difference occurs between the colonized layer and the uncolonized rock substrate. In addition, minor differences between layers in the uncolonized sample strengthen the significance of the variations observed between layers in both of the colonized samples. These results confirm that cryptoendoliths are the architects of mineral weathering within the layers that they inhabit. The

Table 2. Mineral Phases in MM45

Mineral Phase	L1, %	L2, %	L3, %	L4, %
Quartz	26.02	26.88	26.46	26.05
Kaolinite	17.85	17.70	17.06	17.11
Pore space	10.04	8.14	10.32	12.72
Alkali feldspars	46.96	47	46.91	44.69
Total	100.87	99.72	100.69	100.57

results also show that their influence is evident on the layers above and below the layer of habitation.

5. Implications

5.1. Cryptoendoliths as Pioneering Colonists

[37] Endoliths belong to a diverse group of organisms, the lithobionts (from the Greek, lith: rock; bios: life). Lithobionts colonize both rock surfaces and rock interiors in a wide variety of climates and environments. They have been categorized using a combination of topical (location of organism with respect to substrate) and functional criteria, and though this works for many forms, there are also intermediary types. Some, for example, can behave partially as epilithic (surface colonists) and partially endolithic (interior colonists), e.g., lichens; others penetrate carbonate substrates as euendoliths (rock borers) but also colonize preexisting structural cavities, e.g., the green algae *Ostreobium* within corals [Golubic *et al.*, 1981].

[38] Cryptoendoliths are not seen as true rock-boring microbes. They colonize substrates that already have pore spaces, suggesting that they are opportunists. However, they produce oxalic acid, in which silicate minerals are readily dissolved [Sterflinger, 2000]. Therefore, because cryptoendoliths have a mechanism for mineral dissolution, they may be able to inhabit less porous substrates if the substrates can be modified to create more favorable conditions. Cryptoendoliths, then, could act as pioneers, inhabiting a wide variety of substrates that they can weather, resulting in increased porosity and thus habitability of the rocks.

[39] Adaptations of cryptoendolithic microorganisms are not thought to be physiological [Friedmann and Ocampo-Friedmann, 1984a]; they have not, it seems, adapted to the harsh macroenvironment which surrounds them. Instead a morphological adaptation enables them to survive in the protective niches provided by rock interiors [Friedmann *et al.*, 1981]. Narrow, porous air space systems are only accessible to unicellular organisms, and not to lichens that form a mat-like growth structure. Cryptoendolithic lichens have overcome this disadvantage by changing their growth form from mat-like to filamentous in order to gain access to the microscopic pore spaces [Friedmann and Ocampo-Friedmann, 1984a], suggesting that cryptoendolith adaptation has selected for protection from the environment (i.e., gaining access to the interior of rocks) rather than adaptation to the environment itself. Perhaps the necessity to gain

Table 3. Mineral Phases in TP1

Mineral Phase	CR, %	CL, %	RD, %	SB, %
Quartz	70.66	65.44	59.09	45.09
Kaolinite	4	8.73	6.31	10.03
Pore space	14.21	12.82	15.02	15.41
Alkali feldspars	13.67	12.89	19.35	31.00
Total	102.54	99.88	99.77	101.53

Table 4. Mineral Phases in EB1

Mineral Phase	CR, %	CL, %	RD, %	SB, %
Quartz	77.39	81.56	80.05	75.54
Kaolinite	15.46	9.02	15.66	20.42
Pore space	7.71	10.03	4.48	4.36
Total	100.56	100.66	100.19	100.37

access to this important niche could involve the development of more versatile colonization strategies to ensure continuing survival.

[40] The results of this study confirm that cryptoendoliths modify their habitat through the production of oxalic acid, and indicates that over time this directly increases the porosity of their inhabited layer, maximizing the biomass it can support. Whether this capability represents a survival tactic that has arisen by adaptive selection or not, it clearly enables cryptoendoliths to act as pioneers that can modify unsuitable substrates.

5.2. Implications for Putative Martian Cryptoendoliths

[41] Pioneering colonists of a wider variety of substrates would be more successful in extreme environments, and would make better analogues for possible Martian microorganisms if they were able to colonize volcanic rocks, which are prevalent on Mars.

[42] The capacity to create a habitable zone by degradation of feldspars would be an important survival strategy for Martian cryptoendoliths. Conditions of environmental deterioration at certain stages of Mars' history are very similar to the present Antarctic environment, e.g., ~3.1–1.5 Gyr ago where the atmospheric pressure on Mars would have still been high enough to support liquid water (>6.1 mb) but peak air temperatures would not have risen above freezing [McKay *et al.*, 1992]. It would seem likely that symbiotic organisms, such as lichens, that are able to penetrate rocks as pioneers, and establish habitable zones through metabolic production of acids, would be much more likely to survive Martian environmental changes and would have a strong selective advantage over opportunistic organisms, if they had had the opportunity to evolve on Mars. If cryptoendolithic communities did evolve on Mars it would seem likely that survival through to more recent eras would necessitate a pioneering capability.

[43] In addition, the ability of these microorganisms to enhance pore space could augment the colonization of shocked rocks where impact-induced porosity occurs. Cockell *et al.* [2002] have shown endolithic colonization of shock gneisses whereby the microorganisms colonize fissures that are physically linked to the surface of the rocks. Patches of microbial growth then occurs beneath the point of entry with some subsequent lateral invasion of the rock subsurface which appears to be dependant on the extent of shock [Cockell *et al.*, 2002]. The enhancement of pore space generated by the cryptoendolithic microorganisms observed in this study could potentially enable the proliferation of the lateral colonization of the rock, leading to the formation of more coherent colonization bands and a more extensive habitat synonymous to those observed in the Beacon sandstones of Antarctica.

[44] Observations of the mineralogical and chemical alteration of substrates by cryptoendoliths, although undoubtedly not directly applicable to potential Martian ana-

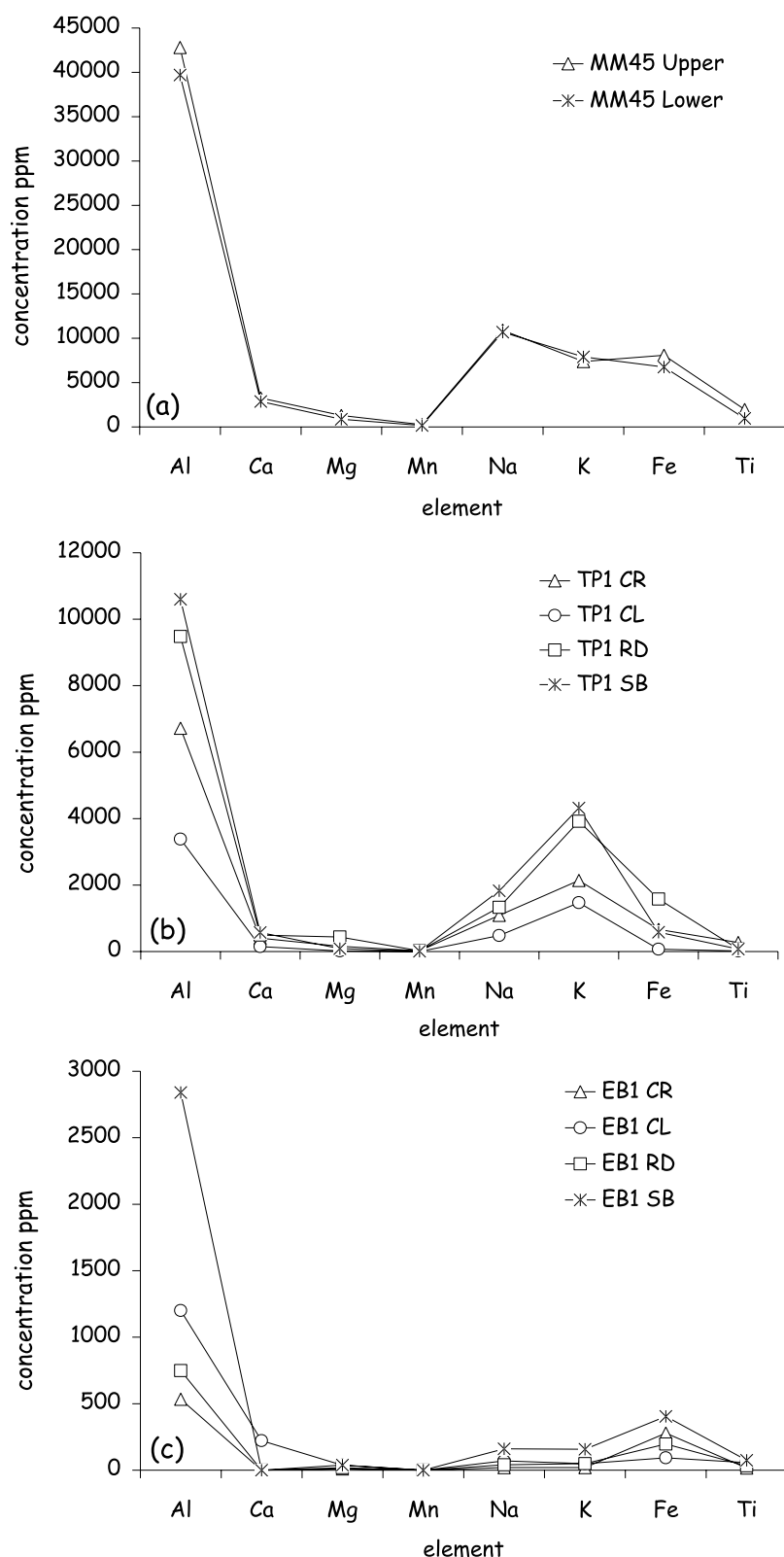


Figure 5. Major elemental concentrations within separate layers in samples. (a) MM45, (b) TP1, and (c) EB1. Errors in element concentration are smaller than the size of the data points.

logues, suggest that cryptoendolithic activity has subtle effects on the surface-correlated mineralogy of inhabited rocks. Aeolian weathering and crust generation is likely to be as important a process on the Martian surface as it is in

the Antarctic. Subtle changes in mineralogy related to enhanced solubility in the presence of biologically produced acids, and exfoliation events may therefore provide potential biomarkers for proof of life on Mars.

[45] Cryptoendolithic lichens may not have played a role in the putative biosphere of an early Mars, however, they may certainly have a role to play in its biological future. The role of lichens in the ecological process of succession on Earth potentially makes them important components in the early stages of ecosynthesis on Mars [Graham, 2004], if such a task were ever undertaken. As the first pioneer species to colonize bare rocks, their growth paves the ways for the establishment of other plants. On Mars they would form an important part of the first microbial ecosystem opening the way for other plants to develop as discussed by Graham [2004]. Cryptoendolithic lichens, with their means of avoiding the harsh external environment, would be particularly valuable. In the Antarctic Dry Valleys, epilithic crustose lichens, prevalent in maritime regions of Antarctica, are absent or rare [Friedmann, 1982]. Having the pioneering capabilities of their epilithic counterparts, but being able to prevail in more hostile environments would make cryptoendolithic lichens an excellent group of microorganisms to include in the first ecosystem on Mars.

6. Conclusions

[46] There are clear mineralogical differences between colonized and uncolonized layers within cryptoendolithic Antarctic sandstones. Results show that cryptoendoliths enhance mineral weathering in their layer of habitation and cause the weathering of minerals through the production of oxalic acid. This dissolves the mineral constituents of the rock. Mobilization and redistribution of elements to other layers creates pore space. The three top layers of colonized sandstones (crust, colonized and iron-rich) are all subject to cryptoendolith influence to varying degrees. It is known that the crust suffers abiogenic aeolian weathering processes that are responsible for both its creation and destruction [Friedmann and Weed, 1987]. However, cryptoendolith-produced oxalic acid interacting with silica may also contribute to the formation of the siliceous crust through the precipitation of amorphous silicates and clay minerals [Johnson and Vestal, 1993].

[47] The layer found just below the colonized layer is affected by cryptoendolith action because it is where iron compounds leached from the inhabited layer are redeposited. Chemical and mineralogical differences between the colonized layer and that of the least altered deeper substrate indicate a biogenic weathering process may be occurring whereby minerals such as feldspars are weathered to clays that may then subsequently be removed, either down through the substrate or upward to the crust.

[48] Rocks in Antarctica are subject to various abiogenic weathering processes. Enhanced biogenic weathering within specific layers occurs in rocks that are colonized by cryptoendolithic microorganisms. The subsequent increase in pore space therefore indicates that cryptoendoliths may be able to pioneer substrates.

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References

- Acasco, C., and J. Wierzbos (2002), New approaches to the study of Antarctic lithobiontic microorganisms and their inorganic traces, and their application in detection of life in Martian rocks, *Int. Microbiol.*, **5**, 215–222.
- Acasco, C., and J. Wierzbos (2003), The search for biomarkers and microbial fossils in Antarctic rock microhabitats, *Geomicrobiol. J.*, **20**, 439–450.
- Blackhurst, R. L., K. Jarvis, and M. M. Grady (2004), Biologically-induced elemental variations in Antarctic sandstones: A potential test for Martian microorganisms, *Int. J. Astrobiol.*, **3**(2), 97–106.
- Cockell, C. S., P. Lee, G. Osinski, G. Horneck, and P. Broady (2002), Impact-induced microbial endolithic habitats, *Meteorit. Planet. Sci.*, **37**, 1287–1298.
- Edwards, H. G. M., N. C. Russell, and D. D. Wynn-Williams (1997), Fourier transform Raman spectroscopic and scanning electron microscopic study of cryptoendolithic lichens from Antarctica, *J. Raman Spectrosc.*, **28**, 685–690.
- Friedmann, E. I. (1980), Endolithic microbial life in hot and cold deserts, *Origins Life*, **10**, 223–235.
- Friedmann, E. I. (1982), Endolithic microorganisms in the Antarctic cold desert, *Science*, **215**, 1045–1053.
- Friedmann, E. I., and R. Ocampo-Friedmann (1984a), Endolithic microorganisms in extreme dry environments: Analysis of a lithobiontic microbial habitat, in *Current Perspectives in Microbial Ecology*, edited by M. J. Klug and C. A. Reddy, pp. 177–185, Am. Soc. for Microbiol., Washington, D. C.
- Friedmann, E. I., and R. Ocampo-Friedmann (1984b), The Antarctic cryptoendolithic ecosystem: Relevance to exobiology, *Origins Life*, **14**, 771–776.
- Friedmann, E. I., and R. Weed (1987), Microbial trace-fossil formation, biogenous, and abiotic weathering in the Antarctic cold desert, *Science*, **236**, 703–705.
- Friedmann, E. I., R. Ocampo-Friedmann, and C. P. McKay (1981), Adaptations of cryptoendolithic lichens in the Antarctic desert, *Colloq. Ecosyst. Subantarct.*, **51**, 65–70.
- Friedmann, E. I., M. Hua, and R. Ocampo-Friedmann (1988), Cryptoendolithic lichen and cyanobacterial communities of the Ross desert, Antarctica, *Polarforschung*, **58**, 251–259.
- Golubic, S., E. I. Friedmann, and J. Schneider (1981), The lithobiontic ecological niche, with special reference to microorganisms, *J. Sediment. Petrol.*, **5**(2), 475–478.
- Graham, J. M. (2003), Stages in the terraforming of Mars: The transition to flowering plants, *AIP Conf. Proc.*, **654**, 1284–1291.
- Graham, J. M. (2004), The biological terraforming of Mars: Planetary ecosynthesis as ecological succession on a global scale, *Astrobiology*, **4**(2), 168–195.
- Johnson, C. G., and J. R. Vestal (1989), Distribution of inorganic species in two Antarctic cryptoendolithic microbial communities, *Geomicrobiol. J.*, **7**, 137–153.
- Johnson, C. G., and J. R. Vestal (1993), Biogeochemistry of oxalate in the Antarctic cryptoendolithic lichen-dominated community, *Microbial Ecol.*, **25**, 305–319.
- McKay, C. P. (1993), Relevance of Antarctic microbial ecosystems to exobiology, in *Antarctic Microbiology*, pp. 593–601, Wiley-Less, New York.
- McKay, C. P., E. I. Friedmann, R. A. Wharton, and W. L. Davies (1992), History of water on Mars: A biological perspective, *Adv. Space Res.*, **12**(4), 231–238.
- Nienow, J. A., C. P. McKay, and E. I. Friedmann (1988), The cryptoendolithic microbial environment in the Ross desert of Antarctica: Light in the photosynthetically active region, *Microbiol. Ecol.*, **16**, 271–289.
- Onofri, S., L. Selbmann, L. Zucconi, and S. Pagano (2004), Antarctic microfungi as models for exobiology, *Planet. Space Sci.*, **52**, 229–237.
- Parnell, J. (2004), Plate tectonics, surface mineralogy, and the early evolution of life, *Int. J. Astrobiol.*, **3**(2), 131–137.
- Russell, N. C., H. G. M. Edwards, and D. D. Wynn-Williams (1998), FT-Raman spectroscopic analysis of endolithic microbial communities from Beacon sandstone in Victoria Land, Antarctica, *Antarct. Sci.*, **10**, 63–74.
- Sterflinger, K. (2000), Fungi as geologic agents, *Geomicrobiol. J.*, **17**, 97–124.
- Sun, H. J., and E. I. Friedmann (1999), Growth on geological timescales in the Antarctic cryptoendolithic microbial community, *Geomicrobiol. J.*, **16**, 193–202.

- Vestal, J. R. (1988a), Primary production of the cryptoendolithic microbiota from the Antarctic desert, *Polarforschung*, *58*, 193–198.
- Vestal, J. R. (1988b), Carbon metabolism of the cryptoendolithic microbiota from the Antarctic desert, *Appl. Environ. Microbiol.*, *54*, 960–965.
- Wierzchos, J., and C. Acasco (2001), Life, decay and fossilization of endolithic microorganisms from the Ross Desert Antarctica: Suggestions for *in situ* further research, *Polar Biol.*, *24*, 863–868.
- Wierzchos, J., and C. Acasco (2002), Microbial fossil record of rocks from the Ross Desert, Antarctica: Implications in the search for past life on Mars, *Int. J. Astrobiol.*, *1*, 51–59.
- Wierzchos, J., C. Acasco, L. G. Sancho, and A. Green (2003), Iron-rich diagenetic minerals are biomarkers of microbial activity in Antarctic rocks, *Geomicrobiol. J.*, *20*, 15–24.
- Wynn-Williams, D. D., and H. G. M. Edwards (2000a), Proximal analysis of regolith habitats and protective biomolecules *in situ* by laser Raman spectroscopy: Overview of terrestrial Antarctic habitats and Mars analogues, *Icarus*, *144*, 486–503.
- Wynn-Williams, D. D., and H. G. M. Edwards (2000b), Antarctic ecosystems as models for extraterrestrial surface habitats, *Planet. Space Sci.*, *48*, 1065–1075.
- Wynn-Williams, D. D., H. G. M. Edwards, E. M. Newton, and J. M. Holder (2002), Pigmentation as a survival strategy for ancient and modern photosynthetic microbes under high ultraviolet stress on planetary surfaces, *Int. J. Astrobiol.*, *1*(1), 39–49.
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